the phase transition the two rings rotate 8·0 and 7·1° in opposite directions away from the position they assume at room temperature. Here the angle between the plane of the polymer backbone and the rings is 72·2°.

Bond lengths and angles are given in Fig. 2. It should be noted that no change in bond lengths and angles can be detected during the course of the phase transition. Obviously, the change in side-chain packing accounts for the different electronic states of the polymer chain, as evidenced by spectroscopic methods. Further investigation of the temperature dependence and the kinetics of the phase change is necessary.

The kind interest Professor Dr G. Wegner took in this investigation is gratefully acknowledged. Calculations were performed at the Rechenzentrum der Universität Freiburg and were supported by the Deutsche Forschungsgemeinschaft.

References

BATCHELDER, D. N. (1976). *J. Polymer Sci., Polymer Phys. Ed.* **14**, 1235.

BATCHELDER, D. N. & BLOOR, D. (1976). *Chem. Phys. Lett.* **38**, 37.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

ENKELMANN, V. & WEGNER, G. (1977). *Makromol. Chem.* In the press.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KOBELT, D. & PAULUS, E. F. (1974). *Acta Cryst.* B**30**, 232–234.

REIMER, G., BÄSSLER, H. & DEBAERDEMAEKER, T. (1977). To be published.

REIMER, G., BÄSSLER, H., HESSE, J. & WEISER, G. (1976). *Phys. Stat. Sol.* (*b*), **73**, 709.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY system – version of March 1976. Tech. Rep. TR 446, Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WEGNER, G. (1972). *Makromol. Chem.* **154**, 35–48.

WILSON, E. G. (1975). *J. Phys. C: Solid State Phys.* **8**, 727–742.

Acta Cryst. (1977). B**33**, 2846–2850

The Crystal and Molecular Structure of Mascaroside, a New Bitter Glycoside from Coffee Beans

BY ARNAUD DUCRUIX AND CLAUDINE PASCARD

Institut de Chimie des Substances Naturelles, CNRS, 91190 *Gif-sur-Yvette, France*

AND MICHÈLE HAMMONNIERE AND J. POISSON

Centre d'Etudes Pharmaceutiques, Université de Paris-Sud, 92290 *Châtenay-Malabry, France**

(*Received* 4 *February* 1977; *accepted* 13 *March* 1977)

The crystal and molecular structure of mascaroside ($C_{26}H_{36}O_{11}$) has been determined by direct methods and X-ray analysis. It crystallizes with two molecules of methanol in the monoclinic system, space group $P2_1$, with cell dimensions: a = 11·752 (6), b = 7·704 (4), c = 16·605 (8) Å, β = 106·68 (5)°, and Z = 2. The intensities were measured by an automatic diffractometer and refinement led to a conventional R value of 6%. The molecule is composed of a diterpene and a β-glucose unit attached to C(17).

Introduction

We report the structure determination of mascaroside. The compound is a bitter principle from beans of Malagasy *Coffea vianneyi* Leroy (Hamonniere, 1974). The very small amount of compound available and chemical difficulties led us to study the structure by X-ray analysis.

A preliminary report of the preparation and structure of the title compound has already been published (Ducruix, Pascard, Hamonniere & Poisson, 1975). Here we give a detailed description of the molecular geometry.

---

* Equipe de Recherche associée au CNRS n° 317.

Experimental

Crystal data

$C_{26}H_{36}O_{11}$, $M_r = 524$, monoclinic, space group $P2_1$, $a = 11·752$ (6), $b = 7·704$ (4), $c = 16·605$ (8) Å, $\beta = 106·68$ (5)°, $V = 1440$ Å^3, $D_m = 1·365$ g cm^{-3}, $Z = 2$, $F(000) = 308$, $\lambda = 1·5418$ Å. The mass difference of 68 was attributed to the presence of solvent, which proved to be two methanol molecules ($D_c = 1·356$ g cm^{-3}).

A Philips PW 1100 diffractometer was used to record the intensities. Each reflexion was measured for $(1·2 + 0·16 \text{ tg } \theta)°$ with a scan speed of 0·02° s^{-1}, and two background measurements for 15 s on each side of the reflexion. Of the 2823 intensities collected, 2006 were above the background ($>2\sigma$). The structure was solved by the direct multi-solution method (Germain, Main & Woolfson, 1971). The glucose moiety appeared on the best E map, and all the heavy atoms were found by a recycling procedure. Full-matrix least-squares refinement of coordinates and isotropic temperature factors led to an R value of 22%.

Table 1. *Fractional coordinates* (× 10^4) *and isotropic thermal parameters*

The molecule of methanol with an occupation factor of 1·0 is indicated by *A* :O*A* (Me)–C*A* (Me). The other molecule, distributed equally between two sites *B* and *C* (occupation factor equal to 0·5), is designated by: O*B*(Me)–C*B*(Me) and O*C*(Me)–C*C*(Me).

	x	*y*	*z*	*B*(Å^2)
C(1′)	2844 (5)	4253 (9)	5252 (4)	2·4
C(2′)	3782 (5)	3383 (9)	4922 (4)	2·7
C(3′)	3204 (6)	2265 (9)	4149 (4)	2·8
C(4′)	2293 (5)	1035 (9)	4344 (4)	2·9
C(5′)	1418 (5)	2082 (9)	4674 (4)	2·6
C(6′)	523 (5)	938 (10)	4910 (4)	3·1
O(cy)	2061 (3)	3013 (6)	5421 (2)	2·5
O(1′)	3437 (4)	5077 (6)	6007 (3)	2·7
O(2′)	4502 (4)	4664 (7)	4685 (3)	3·6
O(3′)	4071 (3)	1238 (7)	3925 (3)	3·2
O(4′)	1667 (4)	118 (9)	3600 (3)	5·1
C(1)	1064 (6)	7137 (11)	9609 (4)	4·0
C(2)	950 (7)	7410 (13)	10463 (5)	4·9
C(3)	1467 (6)	9006 (12)	10860 (4)	4·1
C(4)	2126 (6)	10104 (12)	10560 (4)	3·6
C(5)	2300 (5)	9832 (10)	9700 (4)	2·9
C(6)	3376 (6)	10697 (9)	9558 (4)	3·2
C(7)	3254 (6)	10610 (10)	8614 (4)	3·0
C(8)	3136 (5)	8781 (9)	8251 (4)	2·3
C(9)	2182 (5)	7742 (9)	8528 (4)	2·4
C(10)	2251 (5)	7857 (9)	9484 (4)	2·7
C(11)	2062 (6)	5824 (9)	8196 (4)	3·3
C(12)	3173 (6)	5021 (10)	8022 (4)	3·6
C(13)	4025 (5)	6329 (9)	7787 (4)	2·9
C(14)	4324 (5)	7802 (9)	8446 (4)	2·8
C(15)	2766 (6)	8828 (9)	7262 (4)	2·7
C(16)	3493 (5)	7378 (9)	6976 (4)	2·5
C(20)	3281 (6)	6808 (11)	10080 (4)	3·6
C(17)	2744 (5)	6439 (11)	6242 (4)	3·2
C(18)	2471 (7)	11485 (13)	11136 (4)	4·9
C(19)	2024 (7)	11057 (14)	11810 (5)	5·8
O(2)	464 (5)	6317 (10)	10814 (3)	7·6
O(3)	1402 (5)	9525 (9)	11641 (3)	5·3
O(11)	1098 (4)	5720 (8)	7420 (3)	4·3
O(15)	3014 (4)	10438 (6)	6933 (3)	3·7
O(16)	4496 (4)	8148 (7)	6778 (3)	3·6
O*A*(6′)	−286 (7)	1722 (12)	5210 (15)	3·4
O*B*(6′)	1019 (7)	−199 (12)	5583 (5)	3·4
O*A*(Me)	3190 (5)	6990 (10)	3428 (4)	8·0
C*A*(Me)	3889 (10)	7206 (18)	2807 (6)	9·8
O*B*(Me)	702 (7)	2163 (11)	6871 (5)	2·9
C*B*(Me)	265 (23)	2229 (38)	7590 (17)	11·3
O*C*(Me)	928 (8)	5379 (14)	2556 (6)	4·5
C*C*(Me)	261 (20)	6272 (34)	2941 (14)	8·8

Table 2. *Hydrogen-atom positional parameters* (× 10^3)

	x	*y*	*z*
H(1*a*)	37	773	921
H(1*b*)	101	586	950
H(5)	159	1036	929
H(6*a*)	411	1007	989
H(6*b*)	341	1193	975
H(7*a*)	397	1116	851
H(7*b*)	253	1128	831
H(9)	141	830	823
H(11)	186	508	863
H(12*a*)	290	421	755
H(12*b*)	363	442	854
H(13)	477	572	776
H(14*a*)	456	733	903
H(14*b*)	497	857	837
H(15)	190	854	705
H(17*a*)	245	726	576
H(17*b*)	205	591	638
H(C1′)	240	512	483
H(C2′)	428	262	537
H(C3′)	279	304	367
H(C4′)	272	20	479
H(C5′)	99	292	423

Table 3. *Bond lengths* (Å)

E.s.d.'s in parentheses refer to the last digit.

C(1′)–C(2′)	1·520 (9)	C(5)–C(10)	1·560 (10)
C(1′)–O(cy)	1·409 (8)	C(6)–C(7)	1·535 (9)
C(1′)–O(1′)	1·400 (8)	C(7)–C(8)	1·523 (10)
C(2′)–C(3′)	1·534 (9)	C(8)–C(9)	1·550 (9)
C(2′)–O(2′)	1·427 (8)	C(8)–C(15)	1·574 (9)
C(3′)–C(4′)	1·533 (10)	C(9)–C(10)	1·570 (9)
C(3′)–O(3′)	1·421 (8)	C(9)–C(11)	1·569 (10)
C(4′)–C(5′)	1·527 (9)	C(10)–C(20)	1·553 (10)
C(4′)–O(4′)	1·430 (9)	C(11)–C(12)	1·536 (11)
C(5′)–C(6′)	1·508 (10)	C(11)–O(11)	1·454 (9)
C(5′)–C(cy)	1·445 (8)	C(12)–C(13)	1·533 (10)
C(6′)–O*A*(6′)	1·407 (11)	C(13)–C(14)	1·545 (10)
C(6′)–O*B*(6′)	1·339 (11)	C(13)–C(16)	1·541 (9)
O(1′)–C(17)	1·449 (9)	C(15)–C(16)	1·561 (10)
C(1)–C(2)	1·478 (11)	C(15)–O(15)	1·419 (9)
C(1)–C(10)	1·569 (10)	C(16)–C(17)	1·472 (9)
C(2)–C(3)	1·444 (13)	C(16)–O(16)	1·440 (8)
C(2)–O(2)	1·252 (11)	C(18)–C(19)	1·405 (11)
C(3)–C(4)	1·336 (11)	C(19)–O(3)	1·374 (12)
C(3)–O(3)	1·380 (9)	O*A*(Me)–C*A*(Me)	1·500 (13)
C(4)–C(5)	1·514 (9)	O*B*(Me)–C*B*(Me)	1·431 (29)
C(4)–C(18)	1·410 (12)	O*C*(Me)–C*C*(Me)	1·336 (26)
C(5)–C(6)	1·506 (10)		

Table 4. *Bond angles* (°)

C(10)–C(1)–C(2)	113·9 (6)	C(9)–C(10)–C(5)	106·0 (5)	C(16)–C(17)–O(1′)	109·3 (5)
C(1)–C(2)–C(3)	114·7 (7)	C(9)–C(10)–C(1)	108·9 (5)	O(cy)–C(1′)–C(2′)	110·8 (5)
C(1)–C(2)–O(2)	122·0 (8)	C(9)–C(10)–C(20)	114·8 (5)	O(1′)–C(1′)–O(cy)	108·3 (5)
O(2)–C(2)–C(3)	123·3 (8)	C(5)–C(10)–C(1)	106·9 (5)	O(1′)–C(1′)–C(2′)	107·2 (5)
C(2)–C(3)–C(4)	125·6 (8)	C(5)–C(10)–C(20)	113·0 (5)	C(1′)–C(2′)–C(3′)	110·9 (5)
C(2)–C(3)–O(3)	123·1 (7)	C(1)–C(10)–C(20)	107·0 (5)	C(1′)–C(2′)–O(2′)	110·1 (5)
O(3)–C(3)–C(4)	111·2 (7)	C(9)–C(11)–C(12)	115·8 (6)	O(2′) C(2′)–C(3′)	108·2 (5)
C(3)–C(4)–C(5)	120·9 (7)	C(9)–C(11)–O(11)	109·4 (5)	C(2′)–C(3′)–C(4′)	109·8 (5)
C(3)–C(4)–C(18)	108·0 (7)	C(12)–C(11)–O(11)	107·4 (5)	C(2′)–C(3′)–O(3′)	110·7 (5)
C(18)–C(4)–C(5)	130·8 (7)	C(11)–C(12)–C(13)	116·8 (6)	O(3′)–C(3′)–C(4′)	108·0 (5)
C(4)–C(5)–C(10)	110·2 (6)	C(12)–C(13)–C(14)	108·9 (5)	C(3′)–C(4′)–C(5′)	109·4 (5)
C(4)–C(5)–C(6)	115·7 (5)	C(12)–C(13)–C(16)	115·4 (5)	C(3′)–C(4′)–O(4′)	109·8 (5)
C(6)–C(5)–C(10)	111·9 (5)	C(16)–C(13)–C(14)	100·8 (5)	O(4′)–C(4′)–C(5′)	109·8 (5)
C(5)–C(6)–C(7)	107·7 (6)	C(13)–C(14)–C(8)	101·7 (5)	C(4′)–C(5′) C(6′)	112·1 (5)
C(6)–C(7)–C(8)	114·6 (6)	C(8)–C(15)–O(15)	113·3 (5)	C(4′)–C(5′)–O(cy)	109·3 (5)
C(7)–C(8)–C(9)	110·6 (5)	C(8)–C(15)–C(16)	106·7 (5)	O(cy)–C(5′)–C(6′)	107·4 (5)
C(7)–C(8)–C(15)	111·0 (5)	C(16)–C(15)–O(15)	108·5 (5)	C(5′)–C(6′)–O*A*(6′)	114·2 (6)
C(15)–C(8)–C(14)	101·1 (5)	C(15)–C(16)–C(13)	103·2 (5)	C(5′)–C(6′)–O*B*(6′)	117·1 (6)
C(7)–C(8)–C(14)	113·4 (5)	C(15)–C(16)–O(16)	109·3 (5)	O*A*(6′)–C(6′)–O*B*(6′)	99·2 (7)
C(15)–C(8)–C(9)	108·3 (5)	C(15)–C(16)–C(17)	110·8 (5)	C(1′)–O(cy)–C(5′)	112·0 (5)
C(9)–C(8)–C(14)	112·0 (5)	C(13)–C(16)–O(16)	105·2 (5)	C(4)–C(18)–C(19)	105·3 (7)
C(8)–C(9)–C(10)	116·0 (5)	C(13)–C(16)–C(17)	117·5 (5)	C(18)–C(19)–O(3)	105·7 (8)
C(8)–C(9)–C(11)	112·5 (5)	O(16)–C(16)–C(17)	110·4 (5)	C(19)–O(3)–C(3)	105·8 (6)
C(10)–C(9)–C(11)	112·4 (5)	C(17)–O(1′)–C(1′)	113·3 (6)		

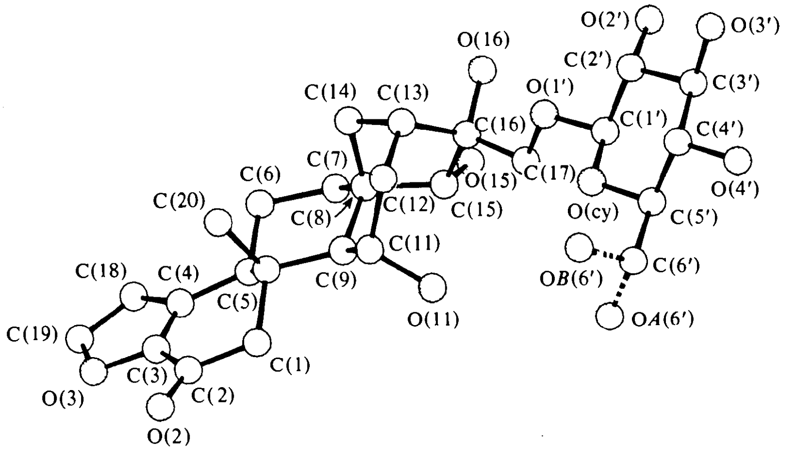


Fig. 1. A perspective view of the molecule of mascaroside.

The first difference series revealed disorder around O(6′), which adopts two positions O*A*(6′) and O*B*(6′) (occupation factors: 0·5), and three molecules of solvent (methanol) (*A*, *B* and *C*); these were introduced into the calculation with occupation factors of 1·0 for one molecule, and 0·5 for the other two. H atoms which could be located at theoretical positions (C–H 1·0 Å, C–$\hat{C}$–H 109°) were also introduced; they were given the same value for *B* as that of the bonded C atoms, and their positions were recalculated at each cycle of refinement.

At the end of the isotropic treatment *R* was 11%. The positional and anisotropic thermal parameters were then refined; the final *R* was 6% for 2006 observed reflexions. The mean δ/σ for the last cycle is 0·3. The atomic scattering factors were those of Doyle & Turner (1968) for C and O, and those of Stewart, Davidson & Simpson (1965) for H. Final atomic parameters are given in Tables 1 and 2, and bond distances and angles in Tables 3 and 4.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32590 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results

The molecule (Fig. 1) is a glucoside formed by a diterpene bonded to the C(1′) atom of the glucose in the *β* position.

The glucose moiety

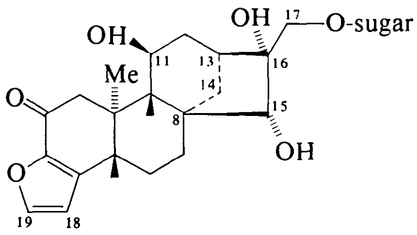
All substituents are in equatorial positions. Bond lengths and angles are in good agreement with those of *β*-glucose (Ferrier, 1963; Chu & Jeffrey, 1968) and cellobiose (Chu & Jeffrey, 1968). The distance C(1′)–O(1′) (1·400 Å) exhibits the noted shortening of the glycosidic bond. The six-membered ring adopts a chair conformation.

Table 5. *Torsion angles* (°)

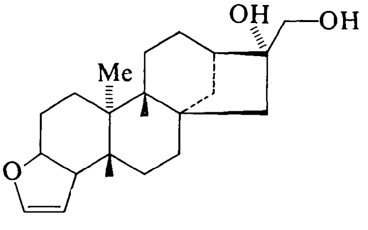
Sugar	
O(cy)–C(1′)–C(2′)–C(3′)	55
C(1′)–C(2′)–C(3′)–C(4′)	−51
C(2′)–C(3′)–C(4′)–C(5′)	54
C(3′)–C(4′)–C(5′)–O(cy)	−59
C(4′)–C(5′)–O(cy)–C(1′)	64
C(5′)–O(cy)–C(1′)–C(2′)	−62
O(cy)–C(5′)–C(6′)–O*A* (6′)	−56
O(cy)–C(5′)–C(6′)–O*B*(6′)	−60
O(cy)–C(1′)–O(1′)–C(17)	−81
C(1′)–O(1′)–C(17)–C(16)	−172
O(16)–C(16)–C(17)–O(1′)	60
Ring *A*	
C(10)–C(1)–C(2)–C(3)	35
C(1)–C(2)–C(3)–C(4)	−8
C(2)–C(3)–C(4)–C(5)	6
C(3)–C(4)–C(5)–C(10)	−30
C(4)–C(5)–C(10)–C(1)	53
C(5)–C(10)–C(1)–C(2)	−58
Ring *B*	
C(10)–C(5)–C(6)–C(7)	65
C(5)–C(6)–C(7)–C(8)	−58
C(6)–C(7)–C(8)–C(9)	49
C(7)–C(8)–C(9)–C(10)	−46
C(8)–C(9)–C(10)–C(5)	51
C(6)–C(5)–C(10)–C(9)	−61
Ring *C*	
C(14)–C(8)–C(9)–C(11)	−50
C(8)–C(9)–C(11)–C(12)	26
C(9)–C(11)–C(12)–C(13)	−28
C(11)–C(12)–C(13)–C(14)	51
C(12)–C(13)–C(14)–C(8)	−70
C(13)–C(14)–C(8)–C(9)	72
Ring *D*	
C(16)–C(13)–C(14)–C(8)	52
C(13)–C(14)–C(8)–C(15)	−43
C(14)–C(8)–C(15)–C(16)	19
C(8)–C(15)–C(16)–C(13)	12
C(15)–C(16)–C(13)–C(14)	−38
Ring *E*	
O(3)–C(3)–C(4)–C(18)	−4
C(3)–C(4)–C(18)–C(19)	3
C(4)–C(18)–C(19)–O(3)	−2
C(18)–C(19)–O(3)–C(3)	0
C(19)–O(3)–C(3)–C(4)	2

The aglycone, $C_{20}H_{24}O_5$

The aglycone part is comprised of a diterpene very similar to cafestol (scheme), isolated from *Coffea arabica* (Djerassi, Cais & Mitscher, 1960) and also present in beans of *Coffea vianneyi.*



Mascaroside



Cafestol

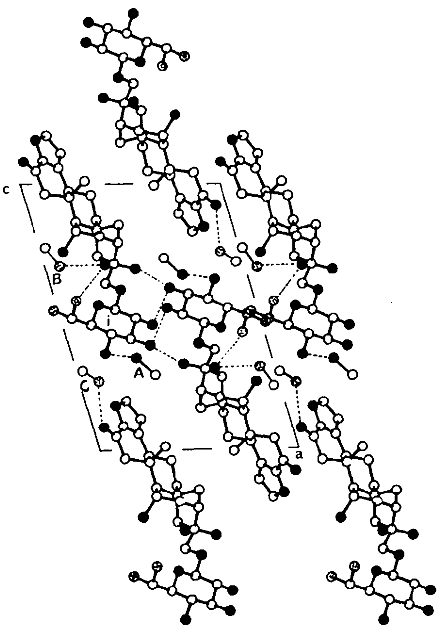


Fig. 2. A projection along **b** showing the packing. Dotted lines represent short intermolecular contacts. Shaded circles are the O atoms of the methanol molecule in the *B* and *C* positions, and O*A*(6′) and O*B*(6′).

These two compounds belong to the family of *trans–anti* pentacyclic diterpenoids of the (–)-kaurene type, in which the *A*/*B* ring fusion is *trans* and the H on C(9) is *β* oriented. The X-ray structure analysis of a bromo derivative of cafestol (Scott, Sim, Ferguson, Young & McCapra, 1962) gave the absolute configuration of cafestol (to which we refer the structure of mascaroside).

Ring *A* has a sofa conformation, with a ketone at C(2), and a furan ring bonded at C(3)–C(4). Rings *B* and *C* have a chair conformation. One hydroxyl group is bonded to C(11) and another to C(15). The *B*/*C* ring junction is *cis*. Ring *D* is linked to C(8) and C(13); it has a half-chair conformation with $\Delta = 8°$ and $\varphi_m = 52°$ (Altona, Geise & Romers, 1968). The atoms forming the furan ring are practically coplanar; the ring has a slight envelope conformation ($\Delta = 27°$, $\varphi_m = 5°$). The torsion angles are given in Table 5.

This diterpene is bonded to the glucose unit through the primary alcohol at C(17).

Packing

The content of the unit cell projected along **b** is represented in Fig. 2. Some of the shortest intermolecular distances, given in Table 6, can be reasonably attributed to hydrogen bonding. The sugar units are certainly bonded to each other through O(2′)···O(3′) along the binary axis. O(15) is most probably hydrogen bonded alternately to O(6′) in one (*B*) of its two positions, and to the hydroxyl group of a methanol molecule also in a statistical site.

Table 6. *Short intermolecular contacts* (Å)

Atom 1 (at x,y,z)	Atom 2	Atom 2 at	
O(cy)	O(15)	x,y,z	3·143 (6)
O(1′)	O(3′)	$1-x, \frac{1}{2}+y, 1-z$	3·033 (6)
O(2′)	O(3′)	$1-x, \frac{1}{2}+y, 1-z$	2·718 (6)
O(3′)	O(16)	$1-x, y-\frac{1}{2}, 1-z$	2·738 (6)
O(4′)	O*A*(Me)	$x, y-1, z$	3·064 (10)
O(2)	O*C*(Me)	$x, y, 1+z$	2·879 (11)
O(15)	O*B*(Me)	$x, 1+y, z$	3·000 (10)
O(15)	O*B*(6′)	$x, 1+y, z$	2·783 (9)
O*B*(6′)	O*A*(6′)	$-x, \frac{1}{2}-y, 1-z$	2·730 (13)

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

CHU, S. C. C. & JEFFREY, G. A. (1968). *Acta Cryst.* B**24**, 830–838.

DJERASSI, C., CAIS, M. & MITSCHER, L. A. (1960). *J. Amer. Chem. Soc.* **81**, 2386–2394.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

DUCRUIX, A., PASCARD, C., HAMMONNIERE, M. & POISSON, J. (1975). *Chem. Commun.* p. 396.

FERRIER, W. G. (1963). *Acta Cryst.* **16**, 1023–1031.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAMMONNIERE, M. (1974). *Café, Cacao, Thé*, **18**, 277–278.

SCOTT, A. I., SIM, G. A., FERGUSON, G., YOUNG, D. W. & MCCAPRA, F. (1962). *J. Amer. Chem. Soc.* **84**, 3187–3199.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.